STUDY OF THE CAUSES OF COLOR IN FOUR SELECTED CRYSTALS OF TOURMALINE FROM THE PEGMATITE OF MATINHA IN DIVINO DAS LARANJEIRAS, MG

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INTRODUCTION

The main cause of the color of minerals is the absorption in the visible electromagnetic spectrum (Burns 1993). In the case of tourmaline several papers are devoted to the mechanisms responsible for the color.The interpretation of the results remains controversial.

Four crystals of tourmaline of different color from the Matinha pegmatite in the Divino das Laranjeiras district, Brazil were selected. They were analyzed using electron microprobe and scanning electron microscope (SEM), Mössbauer effect spectrometry (MS) and optical absorption spectroscopy (both in visible and IR regions).

GEOLOGY

The pegmatite Martinha belongs to the Galileia-Mendes Pimentel Pegmatitic Field, Pegmatite District "Conselheiro Pena", and more precisely to the pegmatitic swarm of Divino das Laranjeiras (Preinfalk *et al*. 2000).

The origin of the gems deposits in the region is related to the granitic rocks genesis episodes (Horn *et al*. 2000). The wall rocks are either the mica-schist of the Rio Doce Group or the granitic source rocks (Figure 1). This strongly folded and deformed mica-schist composed essentially of quartz, muscovite, biotite and feldspar together with s-oriented tourmalines is deeply weathered.

Field observation, petrological studies and mineralogical characterization, permit to precise the composition of the pegmatite that shows essentially weakly developed wall or border zone, some central quartz zones and a matrix formed by quartz, potassic feldspar, white mica and pink, green, red, blue and black tourmalines. In the visible part of the contact zone with the pegmatite, one can observe fragments of mica-schist with small pencil-like crystals of black tourmaline, oriented perpendicularly to the contact.

SAMPLES DESCRIPTION

We selected tourmaline samples from the Matinha Pegmatite due to the occurrence of differently colored species and four tourmaline crystals from this pegmatite were studied:

- MG1, a crystal of green tourmaline;
- MG2, a crystal of pink tourmaline;
- MG3, a zoned crystal of tourmaline with a rose core and green rims;
- MG4, a zoned crystal of tourmaline with a green core and colorless to pink rims.

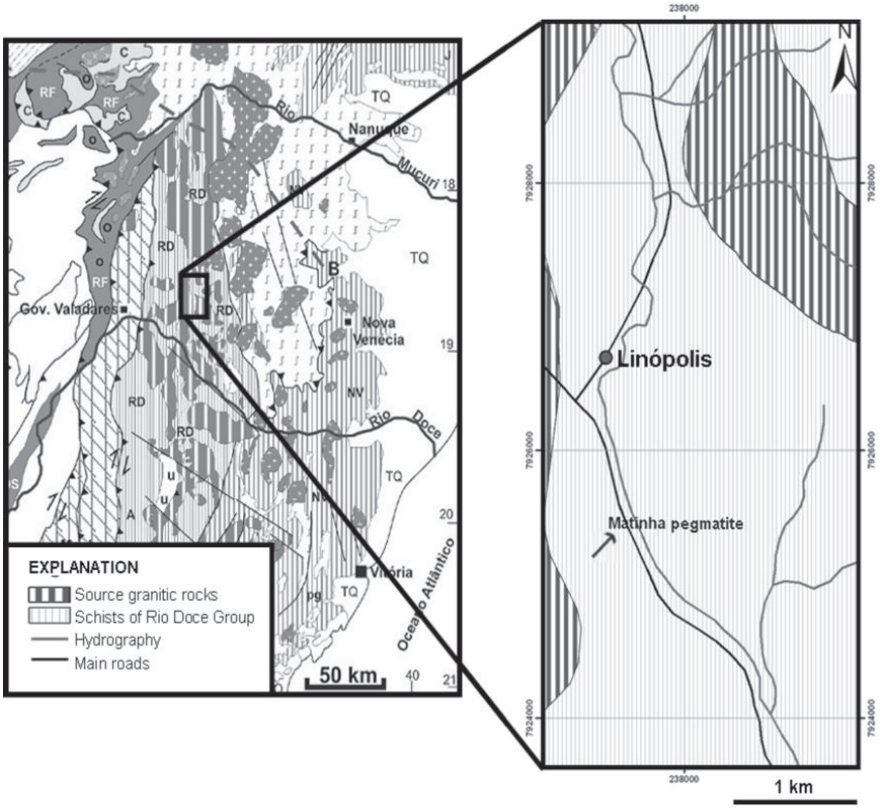

Figure 1 – Geological map in regional and local scales (Pedrosa Soares et al. 2007, modified).

RESULTS

Mössbauer effect spectroscopy

Sample MG1 and the green part of sample MG4 are the only one on which Mössbauer spectrometry could be performed (Figure 2). For others the iron content was too low. Spectra were realised at the GEMAC laboratory (Univ. of Versailles) at room temperature (295K) using a ^{57}Co source and oscillating speeds of respectively 10 and 4 mm/s for MG1 and MG4. Spectra were fitted using the Mossfin program. The isomer shifts show

that Fe is only present as divalent iron (taking in account the detection limit of Mössbauer spectroscopy (~1.5% of total Fe) but is located in different sites of the analysed tourmaline samples. Fe^{2+} is present either in 2 different Y sites (Y1 and Y2) and in the Z site. The attribution of the different doublet to the Y1, Y2, Y3 and Z sites is consistent with the interpretations of Fuchs *et al.* (1998), Andreozzi *et al.* (2008) whereas Dyar *et al.* (1998) assume that the Mössbauer spectroscopy is not able to solve the problem, needing further structural X-ray refinements.

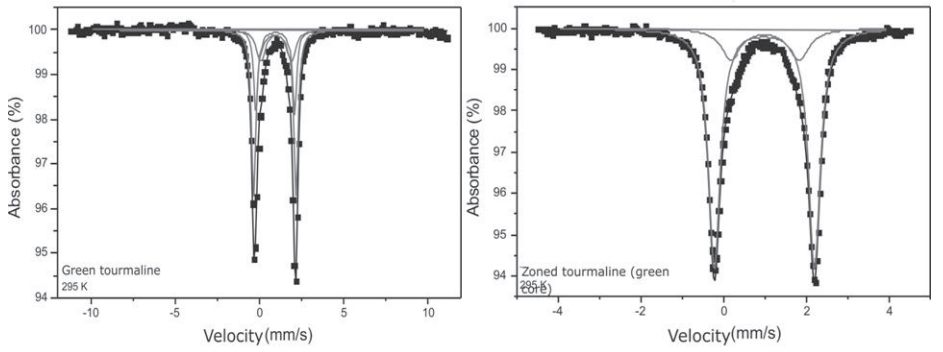

Figure 2 – Left: Mössbauer spectrum for the sample MG 1. Right:. Mössbauer spectrum for the sample MG 4 core.

Optical spectroscopy - UV, visible, IR

Sections were cut parallel to the *c* axis so that the incident beam would be perpendicular to this axis. The thickness of the sections was 12mm for MG1, 57mm for MG2, 33mm for MG 3 and 28mm for MG4. The spectra were performed at the Ecole Polytechnique de Paris, using a CARY 500 spectrometer, with a counting time of 0.2s, a $2cm^{-1}$ step, a non polarized source and at room temperature. Spectra were obtained in the domain between $4,000cm^{-1}$ and $30,000cm^{-1}$ wavenumbers. Spectra were performed on the MG1, MG2, MG3 (core and rim) and MG4 (rim only). Three transition elements are present in the samples (Fe, Mn, Ti) on the basis of analytical results (microprobe, Table 1).

The spectra of the green samples (Figure 3) are characterised by an important absorption band at ~ $13,800cm^{-1}$. The transition $^5T_{2g} \rightarrow {}^5E_g$ of Fe^{2+} seems to be responsible of this band. In the central part of the sample MG4 a band at $9000cm^{-1}$ can be attributed to the splitting of the $13,800\ cm^{-1}$ band. Following the results of Mössbauer spectrometry there is no Fe^{3+} iron present in the sample or only in limited amounts (below 1.5%). Therefore one can observe weak bands between $17,000cm^{-1}$ and $21,000cm^{-1}$ that, following Faye *et al.* (1974) and Smith (1978), should be attributed to charge transfer Fe^{2+}□Fe^{3+}.

Based on the low TiO_2 content (0.01% weight up to 0.03%) and the limited content in FeO the probability of Fe atoms having Ti atoms for neighbour is very low. Therefore as the metal-metal charge transfer between Fe and Ti is particularly intense it is possible that this transition can be recognized at $\sim 23,000cm^{-1}$.

In the pink coloured samples absorption bands (Figure 4) appear between 13,000 and 15,000cm^{-1} and a band at ~19,200cm^{-1}. The band located between 13,000 and 15,000cm^{-1} can be attributed to the $^5T_{2g} \rightarrow {}^5E_g$ transition of Fe^{2+} and the band at approximately 19,200cm^{-1} can be attributed to the $^5E_g \rightarrow {}^5T_{2g}$ transition characterizing Mn^{3+} but for Bershov *et al*. (1969) and also for Smith (1978), this absorption band could be better attributed to an electronic hole. In the spectrum of the sample MG2 two absorption bands at approximately 22,000cm^{-1} and 22,300cm^{-1} could be attributed to forbidden transition of the crystal field of Mn^{3+}.

Table 1 – Average chemical composition in weight % for the four analyzed samples. We can notice the distinction between the rims and the core in the zoned samples (MG 3 and MG 4).

	MG1	MG2	MG3		MG4	
			Rims	Core	Rims	Core
F	1,55	0,96	1,18	1,08	0,93	1,15
Na_2O	2,63	1,76	2,05	1,94	1,79	2,46
MgO	0,02	0,00	0,00	0,00	0,00	0,01
Al_2O_3	35,29	40,70	39,82	41,19	41,02	37,77
SiO_2	35,66	37,88	37,15	37,32	37,27	35,08
K_2O	0,03	0,02	0,02	0,02	0,02	0,03
CaO	0,16	0,48	0,40	0,43	0,43	0,20
TiO_2	0,03	0,02	0,02	0,02	0,02	0,01
MnO	0,61	0,10	1,51	1,21	0,29	0,55
FeO	6,32	0,02	0,41	0,10	0,24	5,30
B_2O_3	12,38	12,18	12,81	12,49	12,66	11,34

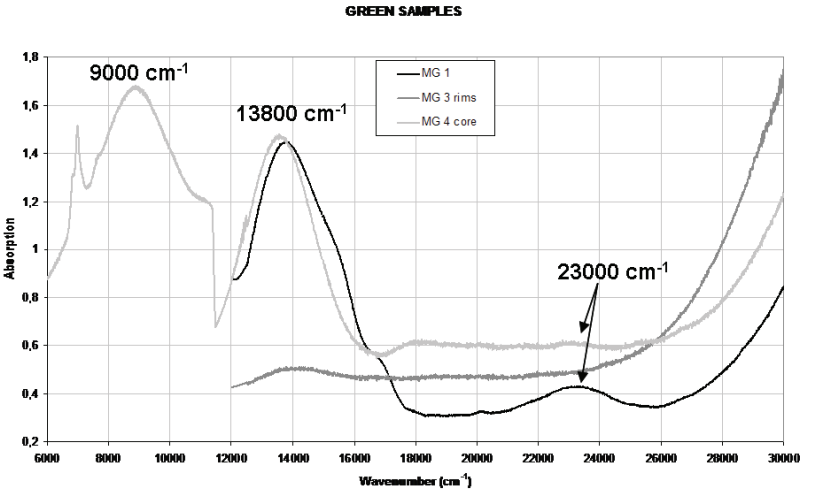

Figure 3 - Green samples spectrograms (MG 1, MG 3 rims and MG 4 core).

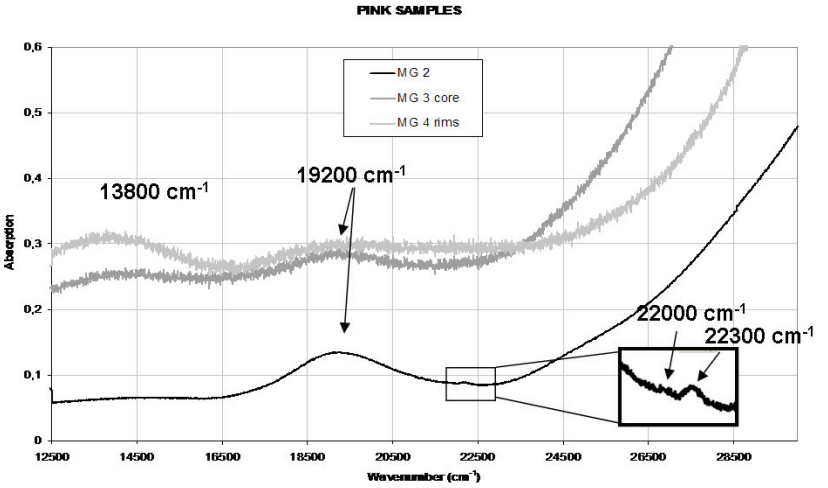

Figure 4 – Pink samples spectrograms (MG 2, MG 3 core and MG 4 rims).

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